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LLNL-TR-678981

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November 5, 2015

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Probing the f -state configuration of URu_2Si_2 with U L_{III} -edge resonant x-ray absorption spectroscopy

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(Dated: February 10, 2015)

I. INTRODUCTION

It has often been said that the most interesting physics occurs when competing interactions are of nearly the same magnitude. Such a situation is surely occurring at URu_2Si_2 's so-called “hidden-order transition”, which garners its name from the missing entropy at a 17.5 K phase transition relative to that expected for a conventional antiferromagnetic phase transition, despite the presence of only a very small ordered magnetic moment.[?] Despite this discrepancy being identified in 1985, the identification of the order parameter remains elusive, although progress toward understanding this transition has been steady since that time, and URu_2Si_2 remains an important research subject today.[?] The work described below provides measures of the $5f$ orbital occupancy and itinerancy using resonant x-ray emission spectroscopy (RXES) at the U L_{III} absorption edge and measuring U $L_{\alpha 1}$ emission that potentially acts as a dividing line between different classes of “hidden-order” theories.

Recent theoretical descriptions fall into two distinct classifications: those that rely on a strongly localized f^2 configuration for the f -orbital,[?] and those that include f -character in the conduction band with a more intermediate f -orbital occupancy.[?] Experimental investigations into these properties generally favor delocalized or partially delocalized $5f$ states. For instance, transport measurements suggest that actinide ions may have localized as well as delocalized $5f$ electrons.[?] The measured band structure and Fermi surface of URu_2Si_2 are well-explained by treating all of the U $5f$ electrons as itinerant. (This may further explain the spin fluctuations observed in inelastic neutron scattering measurements).[?] A possibly confusing factor comes from measurements of the cyclotron resonance, which show an anomalous splitting of the sharpest resonance line under in-plane mag-

netic field rotation, likely caused by the fourfold rotation symmetry of the tetragonal lattice being broken by domain formation, and consistent with the suggestion that there is a nematic Fermi liquid state (where itinerant electrons have unidirectional correlations).[?] Moreover, comparisons of the DC magnetic susceptibility $\chi(T)$ of a system thought to possess a tetragonal singlet crystal field ground state similar to that proposed for URu_2Si_2 show little resemblance.[?]

Although all these measurements are suggestive of a delocalized character for the $5f$ orbital, a direct spectroscopic measurement is required to directly determine $5f$ occupancy and itinerancy. One such measurement is from an electron energy-loss spectroscopy (EELS) experiment which suggest that URu_2Si_2 has $5f$ states which are more localized than α -U (even at room temperature), but still not completely localized, with a $5f$ electron count $n_f \approx 2.7$ suggesting a mixed valence ground state and/or some f -electron itinerancy.[?]

U L_{III} RXES should be able to provide independent confirmation of the EELS result, while potentially also drawing a distinction between a Kondo-like, mixed valence mechanism and a f -band interpretation.

Experimental Setup

RXES data were collected at SSRL wiggler beamline 6-2 using an LN_2 -cooled Si (331) double monochromator calibrated so that the inflection point of a UO_2 reference was at 17166.0 eV. The emission energy was measured using a seven-crystal Ge(777) Johann-type X-ray emission spectrometer, at an emission energy of approximately 13.6 keV, corresponding to the U $L_{\alpha 1}$ edge. Data were collected at room temperature (300 K) and at either 20 K or 30 K for each sample, plus an additional measurement at 15 K for URu_2Si_2 .

II. RESULTS

A. Calculations and measurements on UF_4 and UO_2

In order to consider the f -orbital occupancy and localization features of URu_2Si_2 , comparisons to standard materials are essential. In this case, the standard materials would ideally be ones with strongly localized f -orbitals in the f^2 (tetravalent uranium) and f^3 (trivalent uranium) configurations. From our previous work,⁷ we identified UCd_{11} as possessing strongly localized f electrons and $n_f = 2.73 \pm 0.15$, which is sufficiently close to f^3 to act as a good standard. Unfortunately, there are only a few intermetallics thought to possess a localized f^2 configuration (UPd_3 is a prime example⁷), but we have not succeeded in obtaining data on sufficiently localized intermetallic samples of this type. Instead, we can rely on data from UF_4 as an unquestionably localized f^2 material.

In previous work, we have used UO_2 as a localized f^2 standard, but have recently found it to be a problematic example. UO_2 is considered to be a correlated-electron material and a Mott-Hubbard insulator, and as such, it may have an f occupancy that deviates from two and even have some direct f -band involvement at the Fermi level. More importantly, the ordered cubic symmetry and octahedral coordination of the U-O nearest neighbors generates a substantial crystal field splitting of the unoccupied d states, a situation that is reduced in the more complex monoclinic structure of UF_4 .

This situation is illustrated by the results in Fig. 1 of a 9 atom cluster calculation of the local d density of states using FEFF 9.6.4.⁷ Three curves are shown. In each calculation, only the first shell of 8 oxygen or fluorine atoms are included along with the absorbing uranium atom. A 9 atom cluster was chosen to emphasize the short-range, ligand-field nature of the e_g and t_{2g} features. The UO_2 calculation uses the nominal fluorite structure⁷ and the UF_4 calculation uses the nominal monoclinic structure.⁷ To demonstrate the role of the fluorine atom as opposed to the difference in crystal structure, we also show a calculation on “ UF_2 ”, which is really the same calculation on the same structure as the UO_2 calculation, except all the oxygen atoms were replaced by fluorine.

A number of features are important to discuss with regard to how UO_2 and/or UF_4 make a suitable localized f^2 U L_{III} absorption standard. In all three calculations, there is an e_g state, moving from about -7 eV in UO_2 (with respect to the vacuum energy) to about -5 eV in UF_4 . The t_{2g} state is at a somewhat higher energy, all centered at about 2 eV, with the UF_4 calculation showing a ≈ 1.5 eV split. These calculations therefore demonstrate that the e_g/t_{2g} ligand field splitting is reduced from UO_2 as one moves to the more ionic/less covalent “ UF_2 ” compound and then further to the less symmetric UF_4 compound.

These differences can be seen in the resulting absorp-

tion calculations shown in Fig. 2(a), where we only show the calculations on the “real” UO_2 and UF_4 structures for comparison to actual data shown in Fig. 2(b). One can clearly see the effect of the larger ligand field splitting in the UO_2 calculation and the data compared to those of UF_4 . There are a couple of caveats here. First, there is an extra feature on the lower shoulder in the real absorption data from UF_4 near just below 17170 eV that is not reproduced in the calculation. This feature is considered to be due to a direct $2p_{3/2} \rightarrow 5f$ transition that is quadrupolar rather than dipolar in nature.⁷ Such a feature is not reproduced by FEFF, which doesn’t handle the energetics of the f shells well.

The second caveat is that the calculated Fermi level E_F in these small clusters is about 3 eV lower in UO_2 than the other calculations. This difference persists in calculations with many more atoms in the cluster, up to the largest clusters we tried of about 100 atoms. This is a common problem in FEFF, but may also be a poor reflection of the correlated electron nature of UO_2 , a quality that FEFF cannot capture. This Fermi level shift affects the photoelectron threshold energy, a shift that is not observed experimentally in Fig. 2, so it should be noted that the absorption calculation in Fig. 2(a) is with respect to E_F , rather than with respect to vacuum, in order to make a direct comparison between the calculations and between the calculations and experiment.

The implication of these data and calculations for the purposes of this study is that the ligand field splitting is a complicating factor in the UO_2 spectra when using such spectra to model f^2 behavior in metals where such splitting will be reduced. In contrast, UF_4 appears to be a much better, and less covalent, model for such comparisons. In fact, the ligand field splitting is even less clear in larger cluster calculations of UF_4 , creating an even sharper absorption white line. Therefore, the combination of more ionic bonding (through the replacement of oxygen with fluorine) and reduced symmetry (which further reduces the ligand field splitting) allows UF_4 to be used as a close to ideal localized f^2 absorption standard material.

B. Comparisons between standard materials and URu_2Si_2

RXES data at 300 K for the standard materials and URu_2Si_2 are shown in Fig. 3. The data are discussed first here, and the fit results follow below. First comparing the standard materials, differences are most easily observed and interpreted well below the L_{III} threshold energy. In this method of presenting the data, the data below threshold are toward the bottom of the plot and the features in such data are at a relatively fixed E_t . It is clear from these raw data that the UF_4 and UCd_{11} spectra are both relatively sharp in character, while separated by about 5 eV, consistent with the ≈ 1 eV difference in their f shells. The effect of the ligand field

splitting in UO_2 is pronounced in these data, with a significantly broader spectrum below threshold. It isn't as clear in these plots that the peak emission energy well below threshold is only slightly shifted in UO_2 compared to that of UF_4 , since the UO_2 peak is so much broader and moves visibly as it is resonantly enhanced; the small shift is clearer in the fit results reported below.

The URu_2Si_2 data fall between the limits defined by the UCd_{11} and the UF_4 data, with a significant amount of spectral weight at both extremes. The f^3 weight is even more clearly observed as it becomes resonantly enhanced near $E_i \approx 17166$ eV. It is interesting to compare these results to those from UO_2 , since the energy shift toward UCd_{11} is substantially larger, while the spectra are even broader, in the URu_2Si_2 data compared to the oxide data. Since no large ligand field splitting is expected in the d manifold in URu_2Si_2 , it seems very unlikely that it could be larger in URu_2Si_2 than in UO_2 . These data therefore already strongly suggest an intermediate occupancy of the f orbital, either due to a metallic f band, a Kondo-driven intermediate valence effect, or a mixture of both.

Fits to the URu_2Si_2 data are shown in Fig. 4, and the results of the fits to all the samples are summarized in Table I. The fit quality for all the fits is high, similar to that shown in Fig. 4.

III. DISCUSSION

IV. CONCLUSION

Acknowledgements

Work at Lawrence Berkeley National Laboratory was supported by the Director, Office of Science, Office of Basic Energy Sciences (OBES), of the U.S. Department of Energy (DOE) under contract DE-AC02-05CH11231. X-ray absorption and RXES data were collected at the

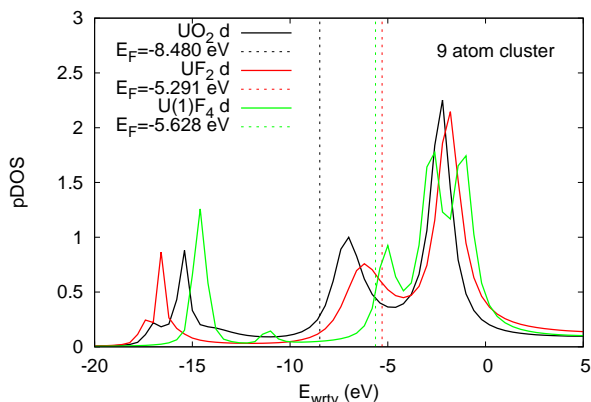


FIG. 1: EXAFS data for UO_2 (black) and UF_4 (red), each collected at

Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the DOE, OBES. Work at Los Alamos National Laboratory was performed under the auspices of the U.S. DOE, OBES, Division of Materials Sciences and Engineering and funded in part by the Lab Directed Research and Development program.

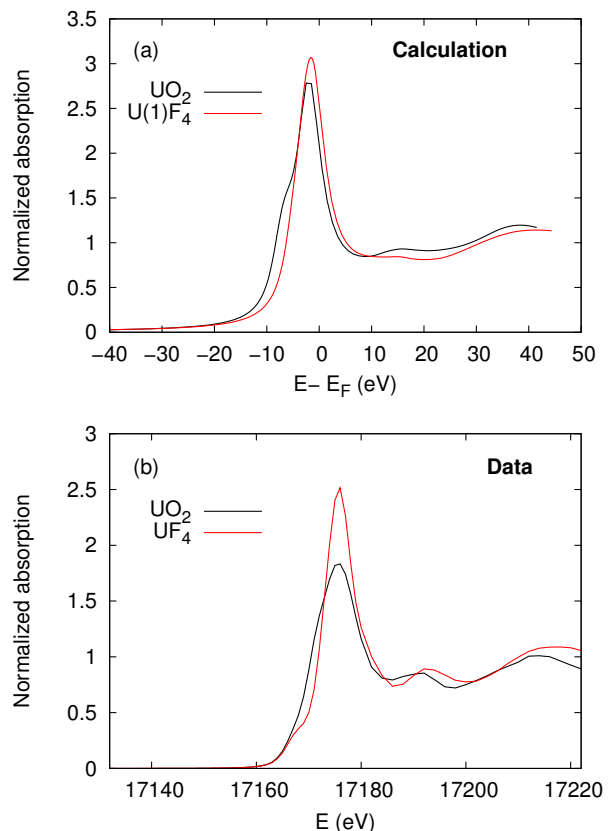


FIG. 2: EXAFS data for UO_2 (black) and UF_4 (red), each collected at

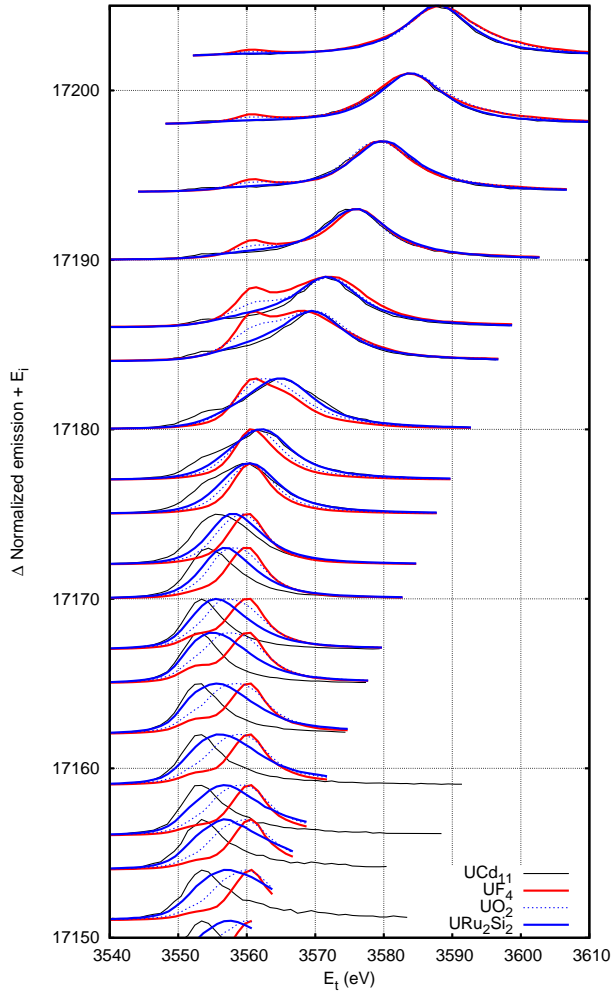


FIG. 3: EXAFS data for UO_2 (black) and UF_4 (red), each collected at

TABLE I: You know you want it... $\Delta E = 7.2$ eV, and E_{gi} is set to the middle peak (f^2) energy.

Compound	E_{gi}	E_{if}	σ_p	f^1 (%)	f^2 (%)	f^3 (%)	n_f
UCd_{11}	17174.3(1)	3559.9(1)	2.1(1)	4(8)	16(9)	81(14)	2.77(15)
UF_4	17174.3(1)	3560.4(1)	1.4(3)	0(6)	96(11)	4(6)	2.0(1)
UO_2	17173.8(1)	3559.8(1)	2.9(3)	0(6)	98(12)	2(6)	2.0(1)
URu_2Si_2	17171.8(1)	3557.7(7)	3.6	20.8	80(3)	14(6)	2(2)

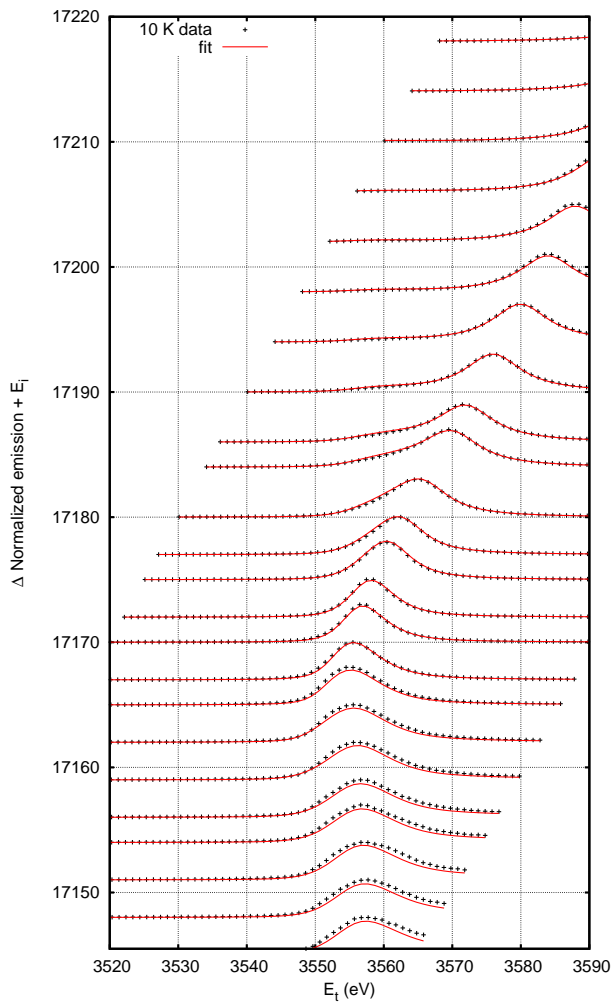


FIG. 4: EXAFS data for UO_2 (black) and UF_4 (red), each collected at